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(54) MODIFIED PARTICLE OF SCALELIKE NATURAL GRAPHITE, ITS PRODUCTION, AND SECONDARY CELL

(57)Abstract:
PROBLEM TO BE SOLVED: To provide modified particles of a scalelike natural graphite comprising spherical particles having a specified structure and characteristics by modifying scalelike natural graphite particles while good properties of the particles are maintained, to provide a producing method of modified particles, and to provide a secondary cell showing a small decrease in the discharge capacity at a large discharge current by using an electrode material comprising the modified particles having good slurry characteristics.
SOLUTION: The modified particles are spherical particles produced by modifying scalelike natural graphite particles into spheres. The spherical particles satisfy the following requirements. The requirements are (a) the sphericity of the particle is >0.86. (b) When fracture plane of the particle is observed with a microscope, it has a cabbage-like appearance with graphite chips projecting in various directions. (c) The peak intensity ratio Ih10/Ih002, which represents the index of randomness of orientation, on the 110 plane (a plane perpendicular to the graphite layer) to the 002 plane (a plane parallel to the graphite layer) by X-ray diffraction analysis is ≥0.0050.

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CLAIMS

[Claim(s)]
[Claim 1] It is the conglobation particle which reformed the scale-like natural-graphite particle so that a globular form might be approached, and this conglobation particle is (a). That circularity is 0.86 or more and (b) In microscope observation of the fracture surface It has the appearance of the shape of a cabbage by which a graphite intercept goes in the various directions, And (c) It is based on the X-ray diffraction method used as the index of the random nature of orientation. 002nd page (field level in a graphite layer) The peak intensity ratios Ih110/Ih002 of the 110th page (field vertical to a graphite layer) are 0.0050 or more, The scale-like natural-graphite refining particle characterized by being what currently is filling all ******.
[Claim 2] tub (1) which has the collision region where jet streams collide, and a floating region using -- feeder (2) from -- tub (1) While teaching a scale-like natural-graphite particle inside tub (1) Opposite nozzle (3) prepared in the lower part side from -- by blowing a jet stream Tub (1) Particles are made to collide in the collision region by the side of the inner lower part, and it is a tub (1). Circulating a particle in the floating region by the side of the inner upper part, on the other hand, the fines below a classification limitation are tubs (1). Classifier prepared in the upper part (4) It is made to discharge out of a tub, And by performing the above-mentioned actuation in batch, it is (a). That circularity is 0.86 or more and (b) In microscope observation of the fracture surface It has the appearance of the shape of a cabbage by which a graphite intercept goes in the various directions, And (c) It is based on the X-ray diffraction method used as the index of the random nature of orientation. 002nd page (field level in a graphite layer) The peak intensity ratios Ih110/Ih002 of the 110th page (field vertical to a graphite layer) are 0.0050 or more, The manufacturing method of the scale-like natural-graphite refining particle characterized by obtaining the conglobation particle which is filling all ******.
[Claim 3] The rechargeable battery which uses the scale-like natural-graphite refining particle of claim 1 as an electrode material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the scale-like natural-graphite refining particle which reformed the scale-like natural-graphite particle which is a raw material so that a globular form might be approached, and its manufacturing method. Moreover, it is related with the rechargeable battery which uses the refining particle as an electrode material.
[0002]
[Description of the Prior Art] a natural graphite -- a raw ore stone -- crushing -- after carrying out secondary crushing, physical or chemical refinement is performed and it usually comes out of purity raising and to grind even to the object grain size further.
[0003] It is related with the object grain size of a natural graphite at grinding of until. The "newest particulate matter process technical collection <the volume on process>, To 275 pages of the chapter of the "graphite" of incorporated company industrial technical pin center,large issuance, and the March, Showa 49 15 first edition 1st ****** per day" [25.] "Probably because friction of particles of what is depended on a friction grinding mold increases by grinding of a fluid energy mold by a particle tending to become flat, the thing of a configuration with the roundness which was able to take the angle is obtained. In grinding of an impact friction mold, since floc is formed that it will be easy to adhere if it becomes impalpable powder 1micro or less, although it progresses well and bulk specific gravity etc. falls, grinding may be felt coarsely seemingly. There is explanation with " and the photograph of gestalt change of the particle by grinding is carried by drawing 25 .3 which are the 274-275 pages.
[0004] JP,8-213020,A and JP,8-298117,A concerning application of these people have disclosure per carrying out jet mill grinding of the scale-like natural graphite, and it is grinding in the example using the Hosokawa Micron micron jet or the counter jet mill made from ARUPINE. According to jet mill grinding, a scale-like natural graphite has explanation that beating is carried out to Sharp with the shape of a scale in these official reports to being crushed in the condition that it crashes and was crushed by the usual grinding methods, such as a ball mill.
[0005] a scale-like natural graphite -- the electrode material of a rechargeable battery -- it can use as a negative-electrode ingredient for lithium secondary batteries especially. When using a scale-like natural graphite for this application, it mixes with a solvent and a binder, a scale-like natural graphite is slurred, and it applies to an object in many cases. In this case, since a scale-like natural graphite has a scale-like (tabular) configuration literally, the fluidity at the time of mixing with a solvent and a binder is bad, in order to acquire predetermined viscosity, the activity of the solvent of a large quantity is needed, and the spreading layer of predetermined thickness may be unable to be formed. Then, in order to improve a fluidity, particle diameter is several micrometers conventionally. The approach of pulverizing, the method of adding various kinds of surfactants and securing a fluidity, the approach of agitating long duration strength, etc. were taken until it became.
[0006]
[Problem(s) to be Solved by the Invention] It of a certain thing from which the thing of the configuration

which has the roundness which was able to take the angle by grinding of a fluid energy mold in the above-mentioned "the newest particulate matter process technical collection <volume on process>" is obtained does not mean smoothing out the edge of a natural-graphite particle in the category of grinding, and does not necessarily mean carrying out like a ball.

[0007] The publication of above-mentioned JP,8-213020,A and JP,8-298117,A also has too the intention of grinding a scale-like natural graphite without losing the shape of a scale in the category of grinding.

[0008] As mentioned above, it is believed by carrying out refining processing of the scale-like natural-graphite particle which is a raw material so that a globular form may be approached although grinding a scale-like natural-graphite particle is known that considering as a conglobation particle is what is not yet known.

[0009] And for the approach of grinding a natural graphite minutely, in order to secure a fluidity when using a scale-like natural graphite as an electrode material of a rechargeable battery, a graphite is 5 micrometers to a slipping and cone sake. The improvement effect fluid with the magnitude beyond it of making it below which is not easy is actually small. And in such a case, it cannot be coped with although making particle diameter small too much depending on an application may be restricted. Although addition of a surfactant has effectiveness in a fluid improvement, selection and the balance of the amount of mixing of a surfactant are difficult for it, and it is common for it to be difficult to hold the continuously optimal condition. Moreover, since addition of a surfactant is restricted depending on an application, it becomes unsuitable at such an application. A required fluidity is not acquired [that it becomes disadvantageous industrially since the method of improving a fluidity by agitating long duration strength requires time amount and an effort, and] by ******** and strong churning of long duration in many cases, either.

[0010] This invention carries out refining processing of it, though the goodness of the scale-like natural-graphite particle which is a raw material is maintained under such a background. The scale-like natural-graphite refining particle which consists of a conglobation particle which has peculiar structure and a peculiar property is offered, It aims at offering the manufacturing method of such a scale-like natural-graphite refining particle, and lowering of the discharge capacity in the big discharge current value using an electrode material with the good slurry property which consists of still such a refining particle offering a small rechargeable battery.

[0011]

[Means for Solving the Problem] The scale-like natural-graphite refining particle of this invention is a conglobation particle which reformed the scale-like natural-graphite particle so that a globular form might be approached, and this conglobation particle is (a). Circularity is 0.86 or more, (b) In microscope observation of the fracture surface, it has the appearance of the shape of a cabbage by which a graphite intercept goes in the various directions, And (c) It is based on the X diffraction (reflection method) used as the index of the random nature of orientation. 002nd page (field level in a graphite layer) The peak intensity ratios Ih110/Ih002 of the 110th page (field vertical to a graphite layer) are 0.0050 or more, It is characterized by being what is filling all ******.

[0012] The manufacturing method of the scale-like natural-graphite refining particle of this invention tub (1) which has the collision region where jet streams collide, and a floating region using -- feeder (2) from -- tub (1) While teaching a scale-like natural-graphite particle inside tub (1) Opposite nozzle (3) prepared in the lower part side from -- by blowing a jet stream Tub (1) Particles are made to collide in the collision region by the side of the inner lower part, and it is a tub (1). Circulating a particle in the floating region by the side of the inner upper part, on the other hand, the fines below a classification limitation are tubs (1). Classifier prepared in the upper part (4) It is made to discharge out of a tub, And by performing the above-mentioned actuation in batch, it is (a). That circularity is 0.86 or more and (b) In microscope observation of the fracture surface It has the appearance of the shape of a cabbage by which a graphite intercept goes in the various directions, And (c) It is based on the X diffraction (reflection method) used as the index of the random nature of orientation. 002nd page (field level in a graphite layer) The peak intensity ratios Ih110/Ih002 of the 110th page (field vertical to a graphite layer) are 0.0050 or more, It is characterized by obtaining the conglobation particle which is filling all ******.

[0013] The rechargeable battery of this invention uses the above-mentioned scale-like natural-graphite refining particle as an electrode material.
[0014]
[Embodiment of the Invention] This invention is explained to a detail below.
[0015] <Scale-like natural-graphite refining particle> The scale-like natural-graphite refining particle of this invention is a conglobation particle which reformed the scale-like natural-graphite particle so that a globular form might be approached, and has satisfied all the following requirements. In addition, (a) Circularity and (b) It explains and the part of the below-mentioned example defines the measuring method of the peak intensity ratios Ih110/Ih002.
(a) Circularity should be 0.86 or more.
(b) Have the appearance of the shape of a cabbage by which a graphite intercept goes in the various directions in microscope observation of the fracture surface.
(c) It is based on the X-ray diffraction method used as the index of the random nature of orientation. 002nd page (field level in a graphite layer) The peak intensity ratios Ih110/Ih002 of the 110th page (field vertical to a graphite layer) should be 0.0050 or more.
[0016] (a) This circularity of the conglobation particle of this invention is 0.88 or more preferably 0.86 or more about ********. Incidentally, the circularity of the scale-like natural-graphite particle which can come to hand in a commercial scene is about 0.84. Since circularity is an index when projecting a particle on a 2-dimensional flat surface, the scale-like natural-graphite particle of a raw material and the conglobation particle of this invention look [approach] numerical, but if circularity goes up, more than it will be expected from the numeric value, conglobation is progressing considerably actually.
[0017] (b) The appearance of ******** is the following (c). Although it is related also to an orientation index, the description of the conglobation particle of this invention is expressed from the appearance. Although it is checked that the graphite intercept has become layer-like only in the same direction mostly by microscope observation, if the scale-like natural-graphite particle in the phase of a raw material is in the conglobation particle of this invention, the graphite intercept is going in the various directions and it has the cabbage-like appearance. If it is in the conglobation particle of this invention, though the layer structure of a scale-like natural graphite is included from this appearance, it turns out that refining of that structure is carried out to the shape of a chimera.
[0018] (c) The conglobation particle of this invention is based on the X diffraction (reflection method) used as the index of the random nature of orientation about a ****** index. 002nd page (field level in a graphite layer) The peak intensity ratios Ih110/Ih002 of the 110th page (field vertical to a graphite layer) are 0.0100 or more still more preferably 0.0080 or more preferably 0.0050 or more. Incidentally, it is 0.0015 to about 0.0018, and its order, and the peak intensity ratios Ih110/Ih002 of the scale-like natural-graphite particle which can come to hand in a commercial scene are notably small as compared with it of the conglobation particle of this invention, and its random nature of orientation is extremely small.
[0019] <Manufacturing method of a scale-like natural-graphite refining particle> Above-mentioned (a), (b) and (c) The scale-like natural-graphite refining particle of this invention which consists of a conglobation particle which is satisfying all requirements can be suitably manufactured industrially by the approach described below.
[0020] namely, tub (1) in which this refining particle has the collision region where jet streams collide, and a floating region using -- feeder (2) from -- tub (1) While teaching a scale-like natural-graphite particle inside tub (1) Opposite nozzle (3) prepared in the lower part side from -- by blowing a jet stream Tub (1) Particles are made to collide in the collision region by the side of the inner lower part, and it is a tub (1). Circulating a particle in the floating region by the side of the inner upper part, on the other hand, the fines below a classification limitation are tubs (1). Classifier prepared in the upper part (4) It is made to discharge out of a tub, And it can manufacture by performing the above-mentioned actuation in batch.

[0021] As a graphite particle which is a raw material, a crystalline high scale-like natural-graphite particle is used. Since this scale-like natural graphite can usually obtain 85 to 99% in the purity of extent

around which it turns a top, if it is required, it can raise purity further with a suitable means.
[0022] In the case of the electrode material of a rechargeable battery, the grain size of the scale-like natural graphite prepared as a raw material is 5-60 micrometers especially about 1-100 micrometers at mean particle diameter, although there is no ********** generally since it changes also with applications. It considers as extent in many cases.
[0023] It is the tub (1) which has the collision region where jet streams collide, and a floating region as equipment for refining of the scale-like natural-graphite particle which is a raw material. It uses. This tub (1) If it carries out, what diverted the fluid bed type counter jet mill in a commercial scene to some other purpose, for example, or improved it for the object of this invention can be used.
[0024] tub (1) Feeder (2) from -- tub (1) A scale-like natural-graphite particle is taught inside. Feeder (2) It is a tub (1) as a hopper type. Installing in a suitable part is desirable and it is a feeder (2) in that case. It can use as output port of a refining particle. Moreover, feeder (2) It is a tub (1) as a screw type. It can also prepare in the lower part. Tub (1) The charge of the scale-like natural-graphite particle inside is a tub (1). Although determined in consideration of an effective tooth space, so much strict nature is not required. However, when there are extremely few charges, floating of a particle is not performed smoothly, but when there are extremely many charges, crushing of a particle becomes excessive and a purposiveness-like refining particle becomes is hard to be obtained.
[0025] tub (1) a lower part side -- a tank wall -- penetrating -- opposite nozzle (3) preparing -- opposite nozzle (3) from -- blowing a jet stream -- tub (1) The particles included in an air current are made to collide in the collision region by the side of the inner lower part. This opposite nozzle (3) It is desirable to allot [two or more] three pieces especially. opposite nozzle (3) from -- conglobation of desired extent is attained by setting up the rate of the jet stream to blow, entrainment capacity, ****, etc. so that a smooth collision and smooth floating can be attained, and setting up an operate time suitably.
[0026] Tub (1) It is a tub (1) although the collision of particles takes place in the collision region by the side of the inner lower part. Circulation of a particle takes place in the floating region by the side of the inner upper part. Setting to a steady state, a particle is a tub (1) in general. It blows up in a core and is a tub (1). It flies down along with the wall time.
[0027] Tub (1) In the upper part, it is a classifier (4). It prepares and the fines below a classification limitation are made to discharge out of a tub. Classifier (4) Usually a high-speed revolution classifier is used. The discharge at this time changes with grain size of the scale-like natural-graphite particle used as a raw material.
[0028] It is important to perform the above-mentioned actuation in batch. It cannot be continuously operated like the usual jet mill grinding, a raw material particle cannot be supplied continuously, and the refining particle made into the object cannot be obtained in having taken out the particle after grinding from the upper part of a tub continuously.
[0029] (a) previously stated by adjusting conditions and performing the above-mentioned actuation, (b) and (c) The conglobation particle with which are satisfied of conditions is obtained.
[0030] <Rechargeable battery> The above-mentioned conglobation particle (scale-like natural-graphite refining particle) can be suitably used mainly as the electrode material of a nonaqueous rechargeable battery, and negative-electrode ingredient especially for lithium secondary batteries. It can use also as electrode materials, such as a polymer battery (paper battery) besides the negative-electrode ingredient for lithium secondary batteries. It can use such for not only an electrode material but for various applications including the constituent particle of a conductive paint, the sliding material for brake discs, and an electroviscous fluid.
[0031] as the positive-electrode ingredient in a lithium secondary battery -- MnO2, LiCoO2, LiNiO2, and LiNi1-yCoyO2, LiMn2O4, and LiMn 2O4 -- LiFeO2 etc. is used. As the electrolytic solution An organic solvent, this organic solvent, and dimethyl carbonate, such as ethylene carbonate, The solution which dissolved electrolytic solution solutes, such as LiPF6, LiBF4, LiClO4, and LiCF3SO3, in the mixed solvent with low-boiling point solvents, such as diethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxyethane, and ethoxymethoxyethane, is used.
[0032] The charge-and-discharge reaction in the case of a lithium secondary battery is as a bottom type

(for the reaction from left part to the right-hand side, a charge reaction and the reaction from the piece of the right to left part are a discharge reaction), and a lithium ion goes back and forth between a positive electrode and negative electrodes.
6C +LiCoO2 = C6Li+CoO2 [0033] <Operation> by performing batch operation using the tub (1) which has the collision region where jet streams collide according to this invention, and a floating region Refining by condensation, adhesion, sticking by pressure, growth, etc. of the particles by collision, grinding the rough edge of the character of grinding etc. is rounded off take place, change of particle size distribution, change of orientation, etc. are brought about as the result, and it is above-mentioned (a), (b) and (c) The conglobated refining particle which satisfies all requirements can be obtained.
[0034] This refining particle has the peculiar random stacking tendency, though the configuration is approaching the globular form and it has a scale-like unit. Therefore, since viscosity is low and a fluidity is maintained, even if the amount of solvents at the time of slurrying is little, and the particle is round and it will not solidify [space will be maintained and] thoroughly even if it is hard to sediment even if it keeps it in the state of a slurry for a long period of time when solid content concentration of a slurry can be made high, and it sediments if a slurry is prepared using this conglobation particle, re-slurrying can attain easily only by performing easy churning at the time of an activity. Moreover, since lowering of the discharge capacity in a big discharge current value becomes small when this is used as a negative-electrode ingredient for lithium secondary batteries, for example, it is suitable as negative-electrode material for a heavy load and high capacity cells (since a load characteristic improves). Though the configuration of a particle being round in the graphite layer applied on the copper foil of an electrode and a particle have a scaly crystal unit, since the stacking tendency has randomized this in one particle, there are many openings, also perpendicularly electrolytic-solution passage is formed at an electrode, and it is thought that migration of a lithium ion will become smooth.
[0035]
[Example] Next, an example is given and this invention is explained further.
[0036] Manufacture [of << refining particle]>>
examples 1-5 and the examples 1-2 of a comparison -- the refining particle was manufactured from the scale-like natural graphite as a raw material as follows.
[0037] <Manufacturing installation> Drawing 1 is the mimetic diagram of the manufacturing installation of the scale-like natural-graphite refining particle used for the experiment. this testing device -- cylinder-like tub (1) it becomes (the dimension is appended to drawing 1). from -- Tub (1) In a lower part side, they are three opposite nozzles (3) (nozzle bore 6.3mm). Opposite arrangement has been carried out so that a core may be turned to (only one only of pieces [them] is shown in drawing 1), and it is a tub (1). In a crowning, it is a classifier (4). The high-speed revolution classifier as an example is arranged. Feeder (2) Tub (1) It has prepared in the side attachment wall and is a tub (1). It pressures upwards at the parallelism ossis occipitalis, and is a nozzle (5). It has prepared.
[0038] <Refining actuation> Mean particle diameter is 20 micrometers with a counter type jet mill about the scale-like natural graphite from China (grain size: 100 meshes of 90% or more passage, and more than purity 99%). Or it ground until it was set to 50 micrometers, and it used as a raw material.
[0039] the above-mentioned raw material particle -- feeder (2) from -- tub (1) while teaching the specified quantity (1kg, 3kg, or 8kg) -- three opposite nozzles (3) respectively -- since -- air was blown, it applied predetermined time and refining processing of a particle was performed. Classifier prepared in the crowning in the meantime (4) About 5 micrometers The following fines were discharged.
[0040] after the above-mentioned actuation -- pressuring upwards -- nozzle (5) from -- air -- sending in -- tub (1) a refining particle -- feeder (2) from -- the conglobation particle (refining particle) made into ejection and the object was obtained.
[0041] <Fracture drawing of a refining particle and external view of a raw material particle> Drawing 2 is fracture drawing (duplicated drawing of the microphotography 5000 times the scale factor of this in which the fracture surface when fixing the conglobation particle obtained in the example 2 with an epoxy resin, and fracturing after frozen solidification with liquid nitrogen was shown) of the conglobation particle (refining particle) of this invention. If it is in the conglobation particle (refining

particle) of this invention, though the graphite intercept has the appearance of the shape of a cabbage which went in the various directions and includes the layer structure of a scale-like natural graphite from drawing 2, it turns out that refining of the structure is carried out to the shape of a chimera.
[0042] On the other hand, drawing 3 is the external view (duplicated drawing of a microphotography 2000 times the scale factor of this) of a scale-like natural-graphite particle used as a raw material. It turns out that the graphite intercept only consists layer-like of drawing 3 only in the same direction mostly if it is in the scale-like natural-graphite particle of a raw material.
[0043] <Circularity of a refining particle> A photograph of a particle is taken for the circularity of the scale-like natural-graphite particle used as the conglobation particle obtained in the example, and a raw material and it is 10 micrometers. About a particle with the above path, it is circularity =(boundary length of considerable circle)/(boundary length of a particle projection image).
When it was alike and having been asked more, the circularity of the conglobation particle of this invention was increasing with 0.88-0.92 to the circularity of the scale-like natural-graphite particle having been 0.84 irrespective of particle size. It is a circle with the projected area as the picturized particle image with the considerable circle same here. The boundary length of a particle projection image is the line length of the border line which connects the edge point of the particle image made binary, and is obtained. Drawing 4 is the explanatory view having shown how to ask for the circularity of a particle and the circumference of the polygon which was able to do the circumference of a black circle with the boundary length of a considerable circle and the white broken line is a boundary length of a particle projection image.
[0044] <Stacking tendency of a refining particle> It is based on the X-ray diffraction method used as the index of the random nature of orientation. 002nd page (field level in a graphite layer) The peak intensity ratios Ih110 'h002 of the 110th page (field vertical to a graphite layer) were preliminary trials, and since the effect about a scan speed and rotational speed had found out the small thing, they measured it the following condition.
[0045]
- Equipment: "RINT2000" by physical science incorporated company
- Cel: bore 2cm, height Restoration of the sample to 0.315cm and a cel: Measure 2g of fine particles and it is a radius. It puts into 1.2cm metal mold, and thickness by 500kg of loads It presses until it is set to 0.315cm.
- Sample consistency: 2.0g / [(1.2) 2cm 2xpix0.315cm] =1.40 g/cm3 (it is the same as the electrode consistency of a cell trial)
- measurement include-angle: -- 3-90 degree and scan speed: -- 9 degrees / min, and number of rotations: -- equipment data-processing: -- integrated-intensity count, nine smoothing mark, and an automatic background cut-off. 002nd page peak (26.5 degrees) 110th page peak (77.5 degrees) From the peak area, it computes by the following formula.
Peak intensity ratio Ih110/Ih002=(net Int field (002))/(net Int field (110)) [0046] consequently, the peak intensity ratio of the scale-like natural-graphite particle of a raw material -- 0. -- as for the peak intensity ratio of the conglobation particle of this invention, it turned out to having been 0015 and 0.0018 that the numeric value is large notably with 0.0072-0.0150, and the random nature of orientation is progressing. Drawing which plotted the relation between a refining operate time and a peak intensity ratio to drawing 5 is shown.
[0047] <Conditions and conclusion of a result> Conditions and a result are collectively shown in the following table 1. In examples 1-2, what performed refining actuation using the raw material particle of the example of a comparison, and examples 3-5 perform refining actuation using the raw material particle of the example 2 of a comparison. It is a tub (1) that it is with air velocity. It is the rate of flow of a bore the part of 250mm. Bulk density puts a particle (30-50g) into a measuring cylinder with a volume of 100 cc, and after it strikes a cylinder wall lightly, it asks for it by measuring the volume.
[0048]
[Table 1]
The example of a comparison / raw material particle An example / refining particle 1 2 1 2 3 4 5 Raw

material charge (kg) - - 1 3 1 8 1 pneumatic pressure (kg/cm2) - - 1 1 1 1 2 air-content (m3/min) - - 2.22.2 2.2 2.2 3.3 air velocity (m/sec) -- 0.75 0.75 0.75 0.75 1.12 Operate time (min) - - 550 15 60 30 Particle diameter (micrometer) 20 50 17 10 45 37 40 circularity (-) 0.84 0.84 0.88 0.90 0.91 0.91 0.92 Bulk density 0.3 (g/cc) 0.50.6 0.8 0.8 0.9 0.9 peak-intensity ratio 0.0015 0.0018 0.0087 0.0150 0.00720.01160.0092 [0049] <Relation between circularity and a refining operate time> About the raw material particle of the example 2 of a comparison, the refining operate time was changed with 10 minutes, 20 minutes, 30 minutes, 40 minutes, and 50 minutes, and the relation between a refining operate time and circularity was investigated. A result is shown in drawing 6 .

[0050] <Rechargeable battery>>

<Assessment of a slurry> In order to see the fitness as a negative-electrode ingredient for lithium secondary batteries, the next experiment was conducted using the raw material particle of the example of a comparison, and the refining particle of an example.

[0051] By carrying out mixed churning of the refining particle 100 weight section obtained in the above-mentioned raw material particle or above-mentioned examples 1-5 of the examples 1-2 of a comparison, the polyvinylidene fluoride 3 weight section as a binder, and the optimum dose of N-methyl pyrrolidone as a solvent The slurry concentration when a slurry is made, in case the viscosity (it measures using a spiral rotational viscometer) of 600cps / 20 degrees C which is the suitable fluid good viscosity for coating actuation is obtained is as follows. When the refining particle of an example was used, it turned out that solid content concentration of a slurry can be made high.

- Raw material particle [-- Refining particle of 35 % of the weight and an example 3 / -- Refining particle of 40 % of the weight and an example 4 / -- Refining particle of 38 % of the weight and an example 5 / -- 38 % of the weight [0052]] of the example 1 of a comparison -- Raw material particle of 26 % of the weight and the example 2 of a comparison -- Refining particle of 30 % of the weight and an example 1 -- Refining particle of 35 % of the weight and an example 2 Thus, when the prepared slurry was gently put for one week on the bottom of a room temperature, the particle was sedimenting and carrying out layer separation of any case, but when the raw material particle of the example of a comparison was used, it compared, and when the refining particle of an example was used, it was able to re-slur easily by easy churning.

[0053] <A coin trial and charge/discharge capability ability> The above-mentioned slurry prepared using the refining particle obtained in the raw material particle and examples 2 and 5 of the examples 1 and 2 of a comparison is applied to copper foil, a press after desiccation is performed, and it is grain density. It adjusted [cc] in 1.4g /, and the trial pole was produced. What stuck the lithium foil to the stainless plate by press are was made into the counter electrode, and it considered as 2 pole type cel. An assembly is the moisture value of 20 ppm. It carries out in the dry box adjusted to below, and is the electrolytic solution. It is LiPF6 to the mixed solvent of 1:1 at a volume ratio with 1 M-LiPF6/(EC+DEC (1:1)), i.e., ethylene carbonate, and diethyl carbonate. What was dissolved at a rate of 1M was used.

[0054] A charge and discharge test is discharge current 0.05C (0.2 mA/cm2), 1.0C (3.7 mA/cm2), and 2.0C (8.0 mA/cm2). It carried out on conditions. Charge is all. It carried out by 0.1 mA/cm2. The result of a charge/discharge capability ability trial is shown in the following table 2. A table 2 shows that it is suitable for a negative-electrode material for that lowering of the discharge capacity in big discharge current value 2C is small in an example, i.e., a heavy load, and high capacity cells.

[0055]

[A table 2]

The discharge current The rate of a capacity factor 0.05C 1.0C 2.0C (%) The example 1 of a comparison 345 280 110 32 The example 2 of a comparison 345 322 142 41 Example 2 345 340 270 78 Example 5 340 310 280 82 # The numeric value of the column of the discharge current is discharge capacity (mAh/g).

Ratio of a capacity factor 100x(discharge capacity of 2.0C)/(discharge capacity of 0.05C).

[0056]

[Effect of the Invention] The scale-like natural-graphite refining particle of this invention has high circularity, and it has the unique appearance of the shape of a cabbage from which a graphite intercept

goes in the various directions in microscope observation of the fracture surface, and is based on the X-ray diffraction method used as the index of the random nature of orientation. 002nd page (field level in a graphite layer) The peak intensity ratios Ih110/Ih002 of the 110th page (field vertical to a graphite layer) are notably high.

[0057] Therefore, even if it makes solid content concentration high at the time of slurrying, it can be made the viscosity suitable for spreading (even if it gets it blocked and lessens the amount of the solvent used), the operability of a slurry is good, and the spreading nature when applying to copper foil etc. and making a plate and a binding property are easy.

[0058] Moreover, since lowering of the discharge capacity in a big discharge current value becomes small when this refining particle is used as a negative-electrode ingredient for lithium secondary batteries, it is suitable for the negative-electrode material for a heavy load and high capacity cells.

[0059] And this refining particle is a tub (1) which has the collision region where jet streams collide, and a floating region. Since it can manufacture easily by using and performing batch operation, it is advantageous also in respect of industrial productivity.

[Translation done.]